Light Induced Intersystem Crossing in $Fe[(py)_3tren](PF_6)_2$ Crystals

H.W.Chong[1] ,A. Cavalleri[1],T.E. Glover[2], R.W. Schoenlein[1], and C.V. Shank[1]
[1]Materials Sciences Division
[2]Advanced Light Source Division
Ernest Orlando Lawrence Berkeley National Laboratory,
University of California, Berkeley, California 94720, USA

INTRODUCTION

$Fe[(py)_3tren]^{2+}$ is a member of a class of octehedrally coordinated iron-based transition metal complexes which undergoes an $\Delta S=2$ spin-crossover transition upon light excitation. This transition proceeds first by electronic excitation from a low-spin singlet ground state to a metal-to-ligand charge transfer state, followed by subsequent relaxation to a high-spin quintuplet state, a process completed within roughly 500 femtoseconds at room temperature. The lifetime of the excited, high-spin state is roughly 700 picoseconds at room temperture, after which the system relaxes back to the singlet ground state. Concomitant with this highly spin-forbidden electronic transition is a structural dilation of the ligand cage surrounding the iron. Current experimental work has only been able to establish a symmetric dilation of the ligand cage in the high-spin state, with the bonds of the first shell of octehedrally-coordinated nitrogen distended by 10% relative to the low-spin state. It has been conjectured, however, that in the intermediary stages of the spin-crossover process, the ligand cage, in fact, distorts asymmetrically, and that it is this distortion which gives energetic preference to the high-spin state. With the ultrashort x-ray pulse capabilities of beamline 5.3.1, we hope to observe dynamically these structural changes in the iron's ligand cage to provide evidence of the role, if any, of the structural changes in the spin-crossover behavior of $Fe[(py)_3tren]^{2+}$.

CURRENT STATUS

We intend to analyze EXAFS and near-edge structures of the iron and nitrogen to determine the atomic motion of the ligand cage as the system evolves after excitation. Due to the signal-limited nature of this experiment, a great deal of effort has gone into the design and characterization of the measurement apparatus. Offline, work has focused on crystal synthesis and sample preparation to provide for optimal signal-to-noise, and optical characterization of the dynamics to determine optimal excitation conditions.

Static spectra of the iron K-edge have been recorded for the candidate molecule and a chemically synthesized high-spin analogue to anticipate the potential spectral changes that may be observed between the two states. These time-independent spectra are shown in Fig. 1 and clearly demonstrate a near-edge shift between the high and low spin states. We intend to next observe similar spectral shifts in a time-resolved fashion following excitation by femtosecond laser pulses.

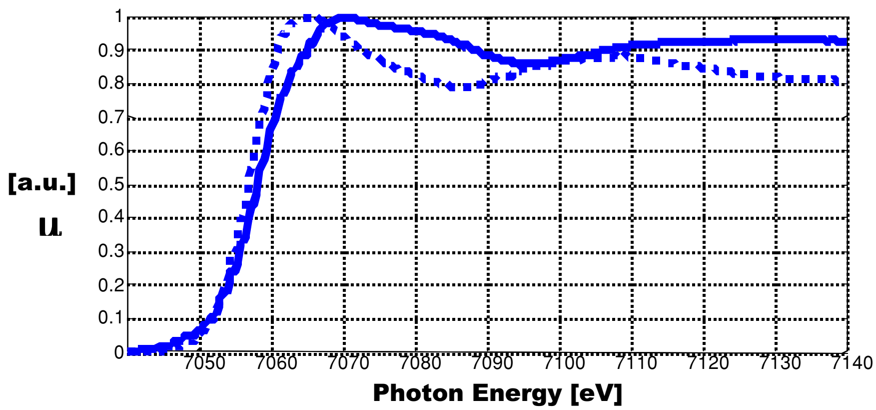

Figure. 1 Static EXAFS spectra of high (dashed line) and low (solid line) spin states of $Fe[(py)_3tren]^{2+}$.

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CONTACT

Principal investigator: Robert Schoenlein, Materials Sciences Division, Ernest Orlando Lawrence Berkeley National Laboratory. Email: rwschoenlein@lbl.gov. Telephone: 510-486-6557.